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(54) Improved multi-layer golf ball

(57) An improved multi-layer golf ball comprises a core, an inner cover layer and an outer cover layer. The inner cover layer is comprised of a high acid ionomer or ionomer blend which may or may not include a filler such as zinc-stearate. The outer cover layer is comprised of a soft, very low modulus ionomer or ionomer blend, or a non-ionomeric thermoplastic elastomer such as polyurethane, polyester or polyesteramide. The resulting multi-layered golf ball of the present invention provides for enhanced distance without sacrificing playability or durability when compared to known multi-layer golf balls.

IMPROVED MULTI-LAYER GOLF BALL

The present invention relates to golf balls and, more particularly, to improved golf balls comprising multi-layer covers which have a hard inner layer and a relatively soft outer layer. The improved multi-layer golf balls provide for enhanced distance and durability properties while at the same time offering the "feel" and spin characteristics associated with soft balata and balata-like covers of the prior art.

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. Consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such

some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, while there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc., a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved impact resistance and carrying distance properties produced by the "hard" ionomeric resins, but also the playability (i.e., "spin", "feel"; etc.) characteristics previously associated

Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides essentially no gain in the coefficient of restitution but provides for the advantageous "feel" and playing characteristics of a balata covered golf ball. Unfortunately, however, while a ball of the '193 patent does exhibit enhanced playability characteristics with improved distance (i.e. enhanced C.O.R. values) over a number of other known multi-layered balls, the ball suffers from poor cut resistance and relatively short distance (i.e. lower C.O.R. values) when compared to two-piece, single cover layer balls. These undesirable properties make the ball produced in accordance with the '193 patent unacceptable by today's standards.

The present invention is directed to new multi-layer golf ball compositions which provide for enhanced coefficient of restitution (i.e, enhanced resilience or carrying distance) and/or durability properties when compared to the multi-layer balls found in the prior art, as well as improved outer cover layer softness

thereby imparting more spin on the ball. As a result, the soft cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability. Consequently, the overall combination of the inner and outer cover layers results in a golf ball having enhanced resilience (improved travel distance) and durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the balls playability properties.

The combination of a high acid ionomer or ionomer blend inner cover layer with a soft, relatively low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic elastomer outer cover layer provides for excellent overall coefficient of restitution (i.e., excellent resilience) because of the improved resiliency produced by the inner cover layer. While some improvement in resiliency is also produced by the outer cover layer, the outer cover layer generally provides for a more desirable feel and high spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Golf Association (U.S.G.A.). Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Patent No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests such as the "nine iron" spin rate test described below in the Examples.

Accordingly, the present invention is directed to an improved multi-layer cover which produces, upon molding each layer around a core (preferably a solid core) to formulate a multi-layer

metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

The inner layer compositions include the high acid ionomers such as those recently developed by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename "Iotek", or blends thereof. Examples of compositions which may be used as the inner layer herein are set forth in detail in copending U. S. Serial No. 07/776,803 filed October 15, 1991, and Serial No. 07/901,660 filed June 19, 1992, both incorporated herein by reference. Of course, the inner layer high acid ionomer compositions are not limited in any way to those compositions set forth in said copending applications. For example, the high acid ionomer resins recently developed by Spalding & Evenflo Companies, Inc., the assignee of the present invention, and disclosed in U.S. Serial No. 07/901,680, filed June 19, 1992, incorporated herein by reference, may also be utilized to produce the inner layer of the multi-layer cover used in the present invention.

The high acid ionomers which may be suitable for use in formulating the inner layer compositions of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or

Surlyn® AD-8422 (sodium cation), Surlyn® 8162 (zinc cation), Surlyn® SEP-503-1 (zinc cation), and Surlyn® SEP-503-2 (magnesium cation). According to DuPont, all of these ionomers contain from about 18.5 to about 21.5% by weight methacrylic acid.

More particularly, Surlyn® AD-8422 is currently commercially available from DuPont in a number of different grades (i.e., AD-8422-2, AD-8422-3, AD-8422-5, etc.) based upon differences in melt index. According to DuPont, Surlyn® AD-8422 offers the following general properties when compared to Surlyn® 8920, the stiffest, hardest of all on the low acid grades (referred to as "hard" ionomers in U.S. Patent No. 4,884,814):

	<u>LOW ACID</u>	<u>HIGH ACID</u>	
	(15 wt% Acid)	(>20 wt% Acid)	
	SURLYN®	SURLYN®	SURLYN®
	<u>8920</u>	<u>8422-2</u>	<u>8422-3</u>
<u>IONOMER</u>			
Cation	Na	Na	Na
Melt Index	1.2	2.8	1.0
Sodium, Wt%	2.3	1.9	2.4
Base Resin MI	60	60	60
HP <sup>1</sup> , °C	88	86	85
FP <sup>1</sup> , °C	47	48.5	45
<u>COMPRESSION MOLDING<sup>1</sup></u>			
Tensile Break,			
psi	4350	4190	5330
Yield, psi	2880	3670	3590
Elongation, %	315	263	289
Flex Mod,			
K psi	53.2	76.4	88.3



Exxon. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

<u>PROPERTY</u>	<u>ESCOR® (IOTEK) 959</u>	<u>ESCOR® (IOTEK) 960</u>
Melt Index, g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, °F	172	174
Vicat Softening Point, °F	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, as a result of the development by the inventor of a number of new high acid ionomers neutralized to various extents by several different types of metal cations, such as by manganese, lithium, potassium, calcium and nickel cations, several new high acid ionomers and/or high acid ionomer blends besides sodium, zinc and magnesium high acid ionomers or ionomer blends are now available for golf ball cover production. It has been found that these new cation neutralized high acid ionomer blends produce inner cover layer compositions exhibiting enhanced hardness and resilience due to synergies which occur during

ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred.

The softening comonomer that can be optionally included in the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high acid ionomers included in the present invention include, but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 30 to about 83% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The new metal cation neutralized high acid ionomer resins are produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200° F to about 500° F, preferably from about 250° F to about 350° F under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in

TABLE 2

<u>Formulation No.</u>	<u>Wt-X Calcium Salt</u>	<u>Wt-X Neutralization</u>	<u>Melt Index</u>	<u>C.O.R.</u>	<u>Shore D Hardness</u>
1(NaOH)	6.98	67.5	0.9	.804	71
2(NaOH)	5.66	54.0	2.4	.808	73
3(NaOH)	3.84	35.9	12.2	.812	69
4(NaOH)	2.91	27.0	17.5	.812	(brittle)
5(MnAc)	19.6	71.7	7.5	.809	73
6(MnAc)	23.1	88.3	3.5	.814	77
7(MnAc)	15.3	53.0	7.5	.810	72
8(MnAc)	26.5	106	0.7	.813	(brittle)
9(LiOH)	4.54	71.3	0.6	.810	74
10(LiOH)	3.38	52.5	4.2	.818	72
11(LiOH)	2.34	35.9	18.6	.815	72
12(KOH)	5.30	36.0	19.3	Broke	70
13(KOH)	8.26	57.9	7.18	.804	70
14(KOH)	10.7	77.0	4.3	.801	67
15(ZnAc)	17.9	71.5	0.2	.806	71
16(ZnAc)	13.9	53.0	0.9	.797	69
17(ZnAc)	9.91	36.1	3.4	.793	67
18(HgAc)	17.4	70.7	2.8	.814	74
19(HgAc)	20.6	87.1	1.5	.815	76
20(HgAc)	13.8	53.8	4.1	.814	74
21(CaAc)	13.2	69.2	1.1	.813	74
22(CaAc)	7.12	34.9	10.1	.808	70

Controls:

50/50 Blend of Ioteks 8000/7030 C.O.R.=.810/65 Shore D Hardness  
 DuPont High Acid Surlyn® 8422 (Na) C.O.R.=.811/70 Shore D Hardness  
 DuPont High Acid Surlyn® 8162 (Zn) C.O.R.=.807/65 Shore D Hardness  
 Exxon High Acid Iotek EX-960 (Zn) C.O.R.=.796/65 Shore D Hardness

low acid ionomers disclosed in U.S. Patent Nos. 4,884,814 and 4,911,451.

Moreover, as a result of the development of a number of new acrylic acid based high acid ionomer resins neutralized to various extents by several different types of metal cations, such as manganese, lithium, potassium, calcium and nickel cations, several new ionomers or ionomer blends are now available for production of an inner cover layer of a multi-layered golf ball. By using these high acid ionomer resins, harder, stiffer inner cover layers having higher C.O.R.'s, and thus longer distance, can be obtained.

More preferably, it has been found that when two or more of the above-indicated high acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further than previously known multi-layered golf balls produced with low acid ionomer resin covers due to the balls' enhanced coefficient of restitution values.

For example, the multi-layer golf ball taught in 4,650,193 does not incorporate a high acid ionomeric resin in the inner cover layer. As will be set forth below in the Examples, the coefficient of restitution of the golf ball having an inner layer taught by the '193 patent (i.e., inner layer composition "D" in the Examples) is substantially lower than the coefficient of restitution of the remaining compositions. In addition, the multi-

method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.

A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale.

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium or lithium salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15-75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and either acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation "Iotek" are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the "Iotek" ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of poly(ethylene-methacrylic acid) some distinct differences in

TABLE 3

Typical Properties of Commercially Available Hard  
Surlyn® Resins Suitable for Use in the Outer Layer Blends of  
the Present Invention

	ASIM D	8960	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gms/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm <sup>3</sup>	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness, Shore D	D-2240	66	64	66	60	62	63
Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23°C) KJ/m <sup>2</sup> (ft.-lbs./in <sup>2</sup> )	D-18225	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Temperature, °C	D-1525	63	62	58	73	61	73

Examples of the more pertinent acrylic acid based hard ionomer resin suitable for use in the present outer cover composition sold under the "Iotek" tradename by the Exxon Corporation include Iotek 4000, Iotek 4010, Iotek 8000, Iotek 8020 and Iotek 8030. The typical properties of these and other Iotek hard ionomers suited for use in formulating the outer layer cover composition are set forth below in Table 4:

<u>Acidic Properties</u>	<u>ASTM Method</u>	<u>Units</u>	<u>7010</u>	<u>7020</u>	<u>7010</u>
Cation type			zinc	zinc	zinc
Melt Index	D-1238	g/10 min.	0.8	1.5	2.5
Density	D-1505	kg/m <sup>3</sup>	960	960	960
Melting Point	D-3617	°C	90	90	90
Crystallization Point	D-3617	°C	--	--	--
Vicat Softening Point	D-1525	°C	60	63	62.5
Weight Acrylic Acid			--	--	--
% of Acid Groups Cation Neutralized			--	--	--
<u>Plaque Properties</u> (3 mm thick, compression molded)	<u>ASTM Method</u>	<u>Units</u>	<u>7010</u>	<u>7020</u>	<u>7030</u>
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	300	420	395
1X Secant modulus	D-638	MPa	--	--	--
Shore Hardness D	D-2240	--	57	55	55

Comparatively, soft ionomers are used in formulating the hard/soft blends of the outer cover composition. These ionomers include acrylic acid based soft ionomers. They are generally characterized as comprising sodium or zinc salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, acrylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably a zinc based ionomer made from an acrylic acid base polymer in an unsaturated monomer of the acrylate ester class. The soft (low modulus) ionomers have a hardness from about 20 to about 40 as measured on



TABLE 5

Physical Properties of Iotek 7520

<u>Property</u>	<u>ASTM Method</u>	<u>Units</u>	<u>Typical Value</u>
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m <sup>3</sup>	0.962
Cation			Zinc
Melting Point	D-3417	°C	66
Crystallization Point	D-3417	°C	49
Vicat Softening Point	D-1525	°C	42

Plaque Properties (2 mm thick Compression Molded Plaques)

Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1 $\frac{1}{2}$ Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebond	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000

In addition, test data collected by the inventor indicates that Iotek 7520 resins have Shore D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of  $3 \pm 0.5$  g/10 min (at 190°C. per ASTM D-1288), and a flexural modulus of about 2500-3500 psi (per ASTM D-790). Furthermore, testing by an independent

neutralized. Based upon FTIR analysis, Iotek 7520 is estimated to be about 30-40 wt.-% neutralized and Iotek 7510 is estimated to be about 40-60 wt.-% neutralized. The typical properties of Iotek 7510 in comparison of those of Iotek 7520 are set forth below:

TABLE 6

Physical Properties of Iotek 7510  
in Comparison to Iotek 7520

	<u>IOTEK 7520</u>	<u>IOTEK 7510</u>
HI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, °F	151	149
Vicat Softening Point, °F	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 90 to about 10 percent hard ionomer and about 10 to about 90 percent soft ionomer. The results are improved by adjusting the range to about 75 to 25 percent hard ionomer and 25 to 75 percent soft ionomer. Even better results are noted at relative ranges of about 60 to 90 percent hard ionomer resin and about 40 to 60 percent soft ionomer resin.

These include, but are not limited to thermoplastic polyurethanes such as: Texin thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane thermoplastic polyurethanes from Dow Chemical Co.; Ionomer/rubber blends such as those in Spalding U.S. Patents 4,986,545; 5,098,105 and 5,187,013; and, Hytrel polyester elastomers from DuPont and Pebax polyesteramides from Elf Atochem S.A.

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core). A comparatively softer outer layer is molded over the inner layer.

The conventional solid core is about 1.545 inches in diameter, although it can range from about 1.495 to about 1.575 inches. Conventional solid cores are typically compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an  $\alpha, \beta$ , ethylenically unsaturated carboxylic acid such as zinc mono or diacrylate or methacrylate. To achieve higher coefficients of restitution in the core, the manufacturer may include fillers such as small amounts of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than those that are needed to achieve the desired coefficient are often included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Other materials may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty

procedures. In the case of the outer cover layer, when a blend of hard and soft, low acid ionomer resins are utilized, the hard ionomer resins are blended with the soft ionomeric resins and with a masterbatch containing the desired additives in a Banbury mixer, two-roll mill, or extruder prior to molding. The blended composition is then formed into slabs and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the high acid ionomer resin compositions used to produce the inner cover layer.

The golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the inner cover layer about wound or solid molded cores to produce an intermediate golf ball having a diameter of about 1.50 to 1.67 inches, preferably about 1.620 inches. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance, solid molded cores are preferred over wound cores.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

#### Examples

Several intermediate balls (cores plus inner cover layers) were prepared in accordance with conventional molding procedures described above. The inner cover compositions were molded around 1.545 inch diameter cores weighing 36.5 grams such that the inner cover had a wall thickness of about 0.0675 inches, with the overall ball measuring about 1.680 inches in diameter.

The cores utilized in the examples were comprised of the following ingredients: high cis-polybutadiene, zinc diacrylate, zinc oxide, zinc stearate, peroxide, calcium carbonate, etc. The molded cores exhibited Riehle compressions of about 60 and C.O.R. values of about .800. A representative formulation of the molded cores is set forth below:

<u>MATERIAL</u>	<u>WEIGHT</u>
BR-1220 (high cis-polybutadiene)	70.70
Taktene 220 (high cis-polybutadiene)	29.30
React Rite ZDA (zinc diacrylate)	31.14
Zinc Oxide	6.23
Zinc Stearate	20.15
Limestone	17.58
Ground Flash	20.15

completely through the cover but that does break the surface. A 3 does not break the surface of the cover but does leave a permanent dent. A 4 leaves only a slight crease which is permanent but not as severe as 3. A 5 represents virtually no visible indentation or damage of any sort.

The spin rate of the golf ball was measured by striking the resulting golf balls with a pitching wedge or 9 iron wherein the club head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110 to 115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

Initial velocity is the velocity of a ball when struck at a hammer speed of 143.8 feet per second in accordance with a test as prescribed by the U.S.G.A.

As will be noted, compositions A, B and C include high acid ionomeric resins, with composition B further including zinc stearate. Composition D represents the inner layer (i.e. Surlyn 1605) used in U.S. Patent No. 4,431,193. Composition E provides a hard, low acid ionomeric resin.

The purpose behind producing and testing the balls of Table IV was to provide a subsequent comparison in properties with the multi-layer golf balls of the present invention.

Table 7

Molded Intermediate Golf Balls

Ingredients of						
<u>Inner Cover Compositions</u>		A	B	C	D	E
Iotek 959	50	50	--	--	--	--
Iotek 960	50	50	--	--	--	--
Zinc Stearate	--	50	--	--	--	--
Surlyn 8162	--	--	75	--	--	--
Surlyn 8422	--	--	25	--	--	--
Surlyn 1605	--	--	--	100	--	--

The goal herein was to use as thin an outer layer as necessary to achieve the desired playability characteristics while minimizing the cost of the more expensive outer materials. However, with a larger diameter final golf ball and/or if the cover is compression molded, a thinner cover becomes feasible.

With the above in mind, an outer cover layer composition was blended together in accordance with conventional blending techniques. The outer layer composition used for this portion of the example is a relatively soft cover composition such as those listed in U.S. Patent No. 5,120,791. An example of such a soft cover composition is a 45% soft/55% hard low acid ionomer blend designated by the inventor as "TE-90". The composition of TE-90 is set forth as follows:

Outer Cover Layer Composition TE-90

Iotek 8000	22.7 weight %
Iotek 7030	22.7 weight %
Iotek 7520	45.0 weight %
White MB <sup>1</sup>	9.6 weight %

<sup>1</sup>White MB consists of about 23.77 weight percent TiO<sub>2</sub>, 0.22 weight percent Uvitex OB, 0.03 weight percent Santonox R, 0.05 weight percent Ultramarine blue and 75.85 weight percent Iotek 7030.

The above outer layer composition was molded around each of the 1.620 diameter intermediate balls comprising a core plus one of compositions A-D, respectively. In addition, for comparison purposes, Surlyn® 1855 (new Surlyn® 9020), the cover composition of the '193 patent, was molded about the inner layer of composition D

acid ionomer resin in the inner layer (i.e. finished balls 1-5). In addition, with the exception of prior art ball 5 (i.e. the '193 patent), resistance to cutting remains good but is slightly decreased. As note above, the prior art ball of the '193 patent suffers substantially in durability (as well as in resiliency) in comparison to the balls of the present invention.

Furthermore, it is also noted that the use of the high acid ionomer resins as the inner cover material produces a substantial increase in the finished balls overall distance properties. In this regard, the high acid ionomer resin inner covers of balls 1-3 produce an increase of approximately 10 points in C.O.R. over the low acid ionomer resin inner covers of balls 4 and about a 25 point increase over the prior art balls 5. Since an increase in 3 to 6 points in C.O.R. results in an average increase of about 1 yard in distance, such an improvement is deemed to be significant.

Several other outer layer formulations were prepared and tested by molding them around the core and inner cover layer combination to form balls each having a diameter of about 1.68 inches. First, B.F. Goodrich Estane® X-4517 polyester polyurethane was molded about the core molded with inner layer cover formulation A. DuPont Surlyn® 9020 was molded about the core which was already molded with inner layer D. Similar properties tests were conducted on these golf balls and the results are set forth in Table VI below:



detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

The qualifications "about" and "substantially" include the precise values, and precise values include values about or substantially the same as the precise values.

The present disclosure includes the foregoing description, and the appended claims, drawings, and abstract.

0.05 inches, the golf ball having an overall diameter of 1.680 inches or more.

5. A golf ball according to claim 1 wherein the inner cover layer has a thickness of about 0.300 inches and the outer cover layer has a thickness of about 0.375 inches, the golf ball having an overall diameter of 1.680 inches or more.

6. A golf ball according to claim 1 wherein the outer layer comprises a low flexural modulus ionomer resin which includes a blend of a hard high modulus ionomer with a soft low modulus ionomer, the high modulus ionomer being a sodium, zinc, magnesium or lithium salt of a copolymer having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms, the low modulus ionomer being a sodium or zinc salt of a terpolymer of an olefin having 2 to 8 carbon atoms, acrylic acid and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms.

7. A golf ball according to claim 6 wherein the outer layer composition includes 90 to 10 percent by weight of the hard high modulus ionomer resin and about 10 to 90 percent by weight of the soft low modulus ionomer resin.

8. A golf ball according to claim 6 wherein the outer layer composition includes 75 to 25 percent by weight of the hard

acrylate ester class having from 1 to 21 carbon atoms, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi.

13. A multi-layer golf ball comprising:

a spherical core;

an inner cover layer molded over said spherical core to form a spherical intermediate ball, said inner cover layer comprising an ionomeric resin including about 17% to about 25% by weight of an alpha, beta-unsaturated carboxylic acid and having a modulus of from about 15,000 to about 70,000 psi;

an outer cover layer molded over said spherical intermediate ball to form a multi-layer golf ball, the outer layer comprising a non-ionomeric thermoplastic selected from the group consisting of polyester elastomer, polyester polyurethane and polyester amide, said outer cover layer having a modulus in a range of about 1,000 to about 30,000 psi.

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**Relevant Technical Fields**

(i) UK CI (Ed.M) C3V (VEM); C3M (MXC)

(ii) Int CI (Ed.5) A63B 37/12; C08L 33/02

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI, CLAIMS, EDOC, WPIL

Search Examiner  
 A J RUDGE

Date of completion of Search  
 26 APRIL 1994

Documents considered relevant  
 following a search in respect of  
 Claims :-  
 ALL

**Categories of documents**

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